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Indoor air quality investigation from screen printing industry

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ABSTRACT

The paper investigates the quality of air in working premises of screen printing in Novi Sad, Serbia. The concentrations of Volatile Organic Compounds, formaldehyde, acetone and ozone were measured in a five screen printing facilities. Measurements were carried out during 4 h, every 40 min, using the air sampler PRO-EKOS AT 401X and mobile gas chromatograph. The sampling position was determined according to the technical characteristics of screen printing desk. Air was sampled from one sampling point as the most suitable in terms of production volume. Determined concentrations of certain gases indicate not only their presence, but also the fact that their level exceeds the prescribed value of the OSHA and NIOSH standards. The concentrations of acetone, isopropanol and methyl ethyl ketone increased from 0.120 to 0.214 ppm within 80 min of printing process in most investigated facilities. The ozone concentrations varied from 0.650 to 3.997 ppm and they differ between facilities almost 1.5 to 6 times depending on intensity of the ventilation, diffusion processes, or interaction with other Volatile Organic Compounds of indoor air. The obtained results confirmed the existence of mutual dependence between pollutants. The regression models determined the quantitative dependence of the studied phenomenon.

Contents

1. Introduction

It is a well known the fact that in the printing process hazardous substances occur in the air, threatening human health. Thus the protection of the working environment is one of important tasks of all employees from management down to the last worker in printing industry. More and more attention is given to the environment protection, so this operation is widely recognized as one of the most serious potential environment risks to human health [1,2]. Indoor air is also important because people spend a substantial proportion of their time in buildings. In residences, day-care centres, retirement homes and other special

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environments, indoor air pollution affects population groups that are particularly vulnerable owing to their health status or age [2].

The printing indoor air can be completely polluted with hazard gases, depending on kind of occurred activities, emissions sources and type of used equipment. Polluted printing indoor air can be connected with employees' health problems [3]. Considering that, the removal of pollutants (VOCs—Volatile Organic Compounds, ozone, acetone, formaldehyde, methyl ethyl ketone, xylene, benzene, toluene, isopropyl alcohol, etc.) became a major requirement among industries [4]. In printing environment there are various emission sources of chemical contaminants, such as VOCs, ozone, and particulate matter. Ozone is a particularly reactive gas and may affect the indoor air quality indirectly through the reaction of high molecular VOCs into formaldehydes, organic acid, and free radicals. Since printing offices have printers and photocopiers, pollutants emitted from printing machines have recently become a serious issue with respect to the indoor air [5–10]. When the workplace environment is considered as a source of ambient air pollution, the type, quantity and way of the chemicals application, as well as the dimensions of facility, ambiental conditions, and the capacity of the aspirators, determine the intensity of chemical pollution of indoor air [11,12]. About 70% of the pollutants classified as hazardous air pollutants (HAPs) are volatile organic compounds (VOCs) [13]. It is therefore important to be able to evaluate the emission of VOCs and ozone from printing facilities and their impact on the indoor environment.

The materials containing HAPs used in the screen printing are the printing inks, coatings, adhesives and cleaning solvents. Other HAPs emission sources of screen printing production include the operations of washing machines, binding and finishing equipment, and some prepress equipment. These pollution sources are generally not significant, but their emissions need to be included in a total facility emission inventory [14].

The emissions of printing air pollutants may affect the indoor environment in several ways: affect health and well-being, give rise to troublesome odors, contaminate other materials, result in discoloration of adjacent materials, and condense on electronic equipment and result in poor production. Indoor pollution caused by VOCs, formaldehyde and ozone is an important aspect of IAQ (indoor air quality) which raises particular concern since many organic indoor pollutants are either known, or are suspected to be allergenic, carcinogenic, neurotoxic, immunotoxic, irritant or indicative of sick building syndrome [15]. Even low concentrations of VOCs (benzene, toluene, xylene, methyl ethyl ketone, acetone, isopropyl alcohol) have been associated with discomfort, irritation and disease [16] including mucous membrane irritation, headache and fatigue [17–19], others are known as carcinogens [20]. The Scientific Committee on Health and Environmental Risks (SCHER) states that formaldehyde (like carbon monoxide, nitrogen dioxide, benzene, naphthalene, environmental tobacco smoke (ETS), radon, lead, and organophosphate pesticides) is a compound of concern in the indoor environment [21,22]. Each of the individual pollutants associated with office equipment has the potential to cause adverse effects if exposures are sufficiently high or if people exposed are sensitive. Therefore it is important to examine the emission sources, but it is associated with difficulties due to the differences between equipment and appropriate techniques in specific printing press. For example, for the same model of printing machine, the emission levels would be affected by some factors such as age, product history, maintenance cycle, air exchange rate, and product loading. Evaluation of emissions control should not only concentrate on one strategy, but also on source control, ventilation, and air cleaning or a combination of these all [23]. Identifying specific constituents of concern can direct efforts to reformulate the raw material (e.g., ink, UV-curing) or make alterations of process that will reduce the emission potential [5]. During the screen printing, printers use organic solvents to clean the excess ink from the screens after printing for the next run or reuse. The cleaners that are used nowadays may contain toxic materials which pose a risk to workers and community members. Virtually all of these pollutants are classified as VOCs [24]. A respectable number of studies about indoor pollution have been conducted so far in residences, schools, hospitals, public buildings, working places, but not in the screen printing facility [25–27].

This paper investigates the quality of air in working premises of screen printing in Novi Sad, Serbia. The investigation is directed to monitoring of potential pollutants (VOCs, ozone, formaldehyde and acetone) in the screen printing press. Analyzed results enable the evaluation of statistical regression model who determine which of the pollutants has the greatest impact on the indoor air and worker′s health. It was the main goal of the paper.

2. Materials and methods

2.1. Site description

Based on preliminary testing of screen printing pollution the highest concentrations of VOCs, acetone, formaldehyde and ozone were found. That was the reason why they were only tested. The concentrations of pollutants were monitored in a five screen printing facilities (SPF 1–5) of Novi Sad, Republic of Serbia. The randomly selected facilities are small with manual production, similar in area (50–70 m^2), number of employees (3–4), production volume (50–70 printing products per hour) and all are unventilated. For example, a scheme of screen printing facility 5 (SPF-5) is presented in Fig. 1. Printing production covers a range of products: labels, folders, planners, posters, lighters and T-shirts. The main equipment of facility was desk with screen holder. The materials mainly used in production process were a porous mesh stretched tightly over a metal frame, paper, cardboard, textile, screen emulsion, screen printing ink, solvent and adhesive.

2.2. Sampling

Air sampling (VOCs, acetone, formaldehyde and ozone) was carried out during one working shift when the printing operations were largest in volume and continuously. In terms of production volume air was sampled from one sampling point as the most suitable. The position of sampling point was determined according to the technical characteristics of screen printing desk.

The VOCs (isopropanol, methyl ethyl ketone, benzene, toluene, xylenes) and acetone were continuously detected in situ for 6 times, once per 40 min, during 4 h by mobile gas chromatograph Voyager (PerkinElmer Photovac Inc). The time of high volume production of one working shift was 4 h.

Batch-sampling methods was performed for formaldehyde and ozone. Formaldehyde and ozone were continuously sampled during 4 h using air sampler PRO-EKOS AT. 401X. Air sampler was placed at a height of 1.3 m from the floor and 2.4 m distance from the screen printing desk. The indoor air was infiltrated through the Drechsel bottles with diffuser frit containing absorption indicator solutions for ozone (1% potassium iodide in 0.1 M sodium hydroxide) and formaldehyde (95 cm^3 concentrated sulfuric acid and 0.5 cm^3 1% hromotropic acid). The air flow was 0.5 dm^3/min and 0.2 to 0.4 dm^3/min for formaldehyde and ozone, respectively.

2.3. Methods

2.3.1. VOCs determination by mobile gas chromatography

Standard of investigated pollutants (acetone, isopropanol, methyl ethyl ketone, benzene, toluene, xylenes) was used for the calibration and quantification of VOCs. Supelcowax 10–polyethylene glycol (PEG)

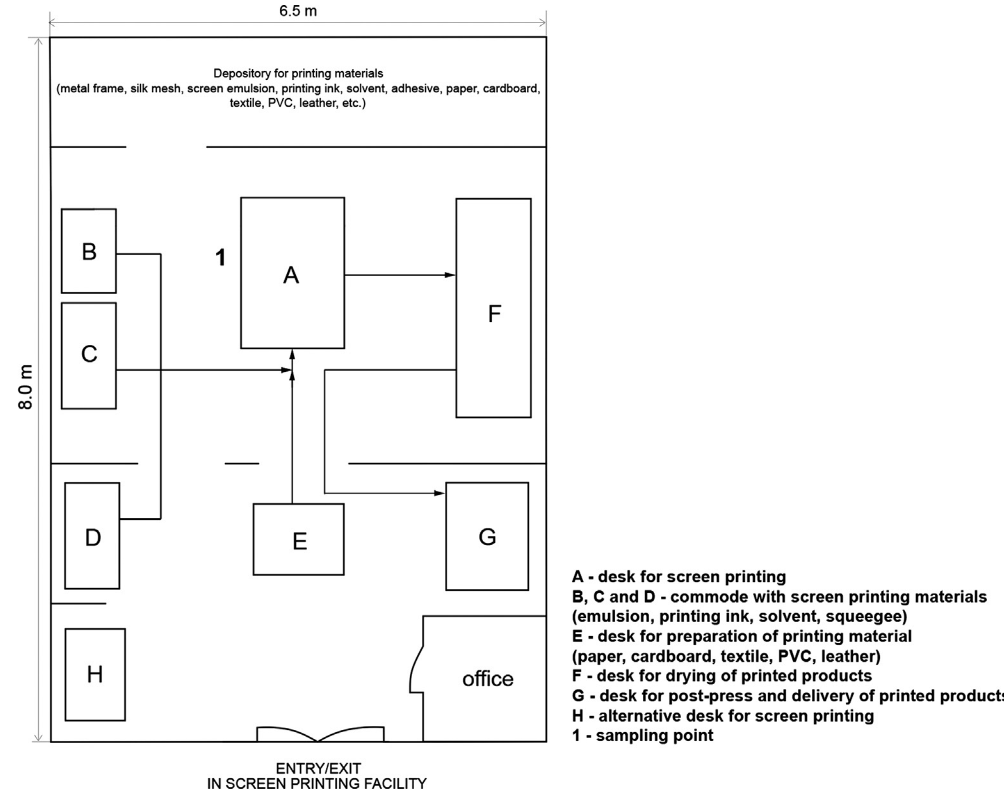


Fig. 1. A scheme of screen printing facility 5 (SPF 5).

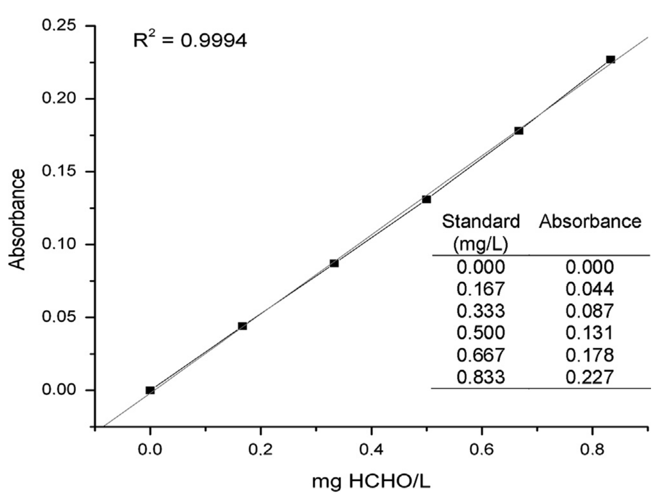


Fig. 2. Calibration curve for formaldehyde.

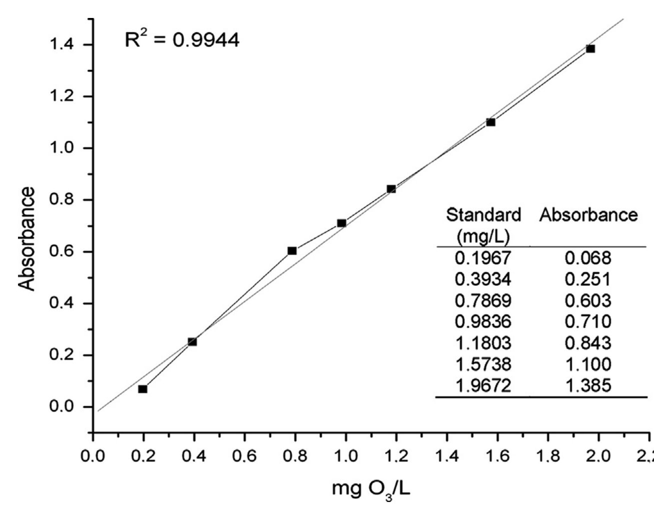
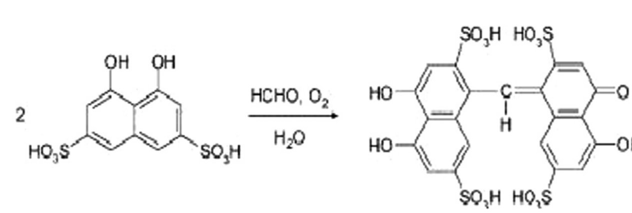


Fig. 3. Calibration curve for ozone.

column was used to separate the sampled components. The separated compounds were detected by the photoionization detector. The target VOCs were identified by unique gas chromatography retention times, compared with working standards. The VOCs (individual and total) were sampled and detected in situ for 6 times, once per 40 min, during 4 h by mobile gas chromatograph Voyager (PerkinElmer Photovac Inc). The detection limit of device was 0.001 ppm.



2.3.2. Formaldehyde determination by UV/VIS spectrometry

In the presence of concentrated sulfuric acid, chromotropic acid (1,8 dihydroxynaphthalene-3,6-disulfonic acid) reacts with formaldehyde to give a red-violet hydroxydiphenylmethane derivative (reaction (1), [28]).

The resulting chromophore was analyzed by UV/VIS spectrometry at 580 nm (UV/VIS spectrophotometer DR 5000 HACH LANGE). The concentrations of formaldehyde were determined from calibration curve using the standard formaldehyde solution of 1 mg/L [29] Fig. 2. Based on determined formaldehyde concentrations from calibration

curve and the amount of air transmitted through the absorbing solution, unknown formaldehyde concentrations were calculated using Eq. (1):

$$\text{mg HCHO}/L = \frac{(\text{mg}/L\ \text{HCHO}) \times 1000}{V} \quad (1)$$

where V is volume of air sampled.

2.3.3. Ozone determination by UV/VIS spectrometry

Ozone was determined using the UV/VIS spectrometry method based on the complex formation between phosphorus-sulfamine reagent and standard iodine solution. The absorbance of created yellow-colored complex is determined by UV/VIS spectrometry at 352 nm (UV/VIS spectrophotometer DR 5000 HACH LANGE) [10]. Based on determined ozone concentrations from calibration curve, Fig. 3, and amount of air transmitted through the absorbing solution, unknown ozone concentration was calculated using Eq. (2):

$$\text{mg } O_3/L = \frac{(\text{mg}/L\ \ O_3) \times 1000}{V} \quad (2)$$

where V is volume of air sampled.

2.3.4. Multiple linear regression analysis

Multiple linear regression attempts to model the relationship between two or more explanatory variables and a response variable by fitting a linear equation to observed data. Every value of the independent variable X is associated with a value of the dependent variable Y. All observed variables are random. The statistical calculations were made by ORIGIN 5.0. software package, as the most suitable.

Admittedly, regression is a statistical method that describes the relationship between different phenomena. Importance of this method lies in the ability to predict the outcome of certain events based on knowledge of other phenomena. Phenomena on which the prediction is obtained, $X_1, X_2,\ldots, X_k$, population, are independent (deterministic) variables or factors and their occurrence depend on these variables, Y is called the dependent (stochastic) variable. The dependence of these phenomena is given in population regression model (Eq. (3)):

$$Y = P_Y(X_1,\ldots,X_k) + E, \quad P_Y \text{ everywhere replaced by } \mu \quad (3)$$

where E is the random error.

Due to predict the outcome of certain events, the function defining the interdependent variables should be found. For multiple linear regressions, regression function of the population is the following (Eq. (4)):

$$P_Y(X_1, X_2, \ldots, X_k) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \cdots + \beta_k X_k \quad (4)$$

where β_i, $i=0,\ldots, k$ is unknown regression coefficient, X_j, $j=1,\ldots, k$ is independent deterministic variable.

The difference between the actual value of the dependent factor Y and predicted values of the population is prediction error. Mistakes are almost always different from 0, so it is necessary to find the function for which they are minimal [30–33].

3. Results and discussion

The time variation of indoor VOC concentrations is shown in Table 1. In the screen printing facility 1 (SPF 1) concentrations of acetone, isopropanol and methyl ethyl ketone slightly increased from 0.120 to 0.214 ppm within the 80 min of printing process. Printing facility 2 (SPF 2) has the highest concentration of all pollutants after 240 min of printing, SPF 3 after 200 min and SPF 4 has the highest concentration within 120 min of printing. These differences are most likely caused by the production of various products. In the case of SPF 5, *p,m*-xylene has the highest values, because the facilities have a variety of high volume of circulation. The character of indoor pollutants in screen printing process is given in Fig. 4.

The concentrations of indoor air pollutants in SPF 3 were larger than in all other facilities just like the ozone measuring (Table 2), therefore ozone and VOCs were transferred at the head of printers, riding an up current of hot air.

Table 1
The time variation of indoor VOC concentrations.

Screen printing facility	Substances	Concentration (ppm) Sampling time (min)					
		40	80	120	160	200	240
SPF 1	Acetone	0.125	0.127	0.096	0.106	0.095	0.113
	Isopropanol	0.107	0.120	0.113	0.117	0.097	0.119
	Methyl ethyl ketone	0.206	0.214	0.120	0.174	0.126	0.186
	TVOCs	0.438	0.461	0.329	0.397	0.318	0.418
SPF 2	Toluene	–	0.238	0.592	–	–	–
	Ethylbenzene	0.053	0.896	1.703	1.822	1.905	2.008
	p,m-xylene	2.566	4.977	6.438	7.540	9.200	10.931
	o-xylene	0.024	0.699	0.982	0.993	1.034	1.104
	Isopropanol	–	–	–	0.089	0.102	0.107
	Acetone	0.065	0.087	0.096	0.122	0.135	0.187
	Methyl ethyl ketone	0.099	0.157	0.209	0.212	0.238	0.253
	TVOCs	2.807	7.054	10.020	10.778	12.614	14.590
SPF 3	Benzene	–	–	–	0.130	–	–
	Toluene	0.422	0.693	2.237	23.700	172.000	13.700
	TVOCs	0.422	0.693	2.237	23.830	172.000	13.700
SPF 4	Acetone	0.021	0.037	–	0.017	–	–
	Isopropanol	0.144	0.016	0.058	0.043	–	0.103
	Toluene	0.920	0.437	25.100	1.182	0.311	1.176
	TVOCs	1.085	0.490	25.158	1.242	0.311	1.279
SPF 5	Toluene	0.023	0.187	0.322	0.431	0.466	0.591
	Ethylbenzene	0.255	0.287	0.341	2.522	5.188	7.347
	p,m-xylene	0.940	1.733	2.496	9.600	27.340	67.800
	o-xylene	0.032	0.101	0.136	0.764	1.650	3.269
	Isopropanol	0.104	0.198	0.226	0.203	0.192	0.187
	Acetone	0.078	0.121	0.146	0.432	0.569	0.949
	Methyl ethyl ketone	0.105	0.188	0.238	0.202	0.194	0.209
	TVOCs	1.537	2.815	3.905	14.154	35.599	80.352

Note: Dash (–) represents the concentrations below the threshold detectable limit.

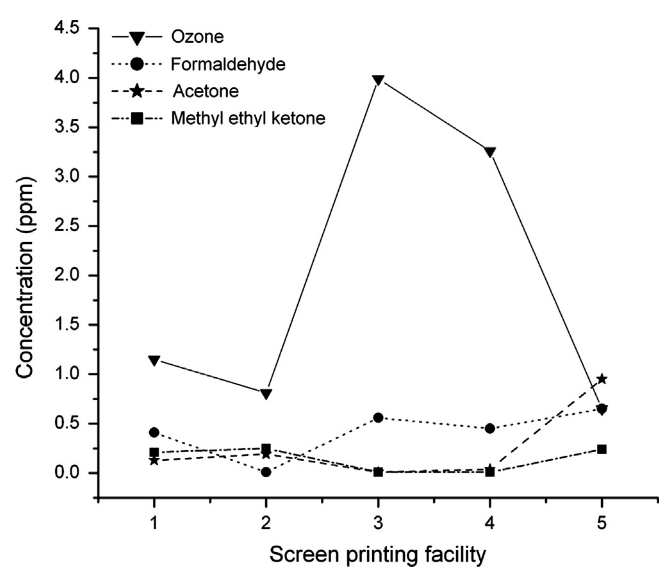


Fig. 4. Character of the indoor air pollutants in screen printing process.

Table 2
Average exposure concentrations, individual and additive effects of HAPs in screen printing facilities.

Screen printing facility	Substances	AEC (ppm)	Individual effect	Additive effect
SPF 1	Acetone	0.110	0.11×10^{-3}	0.55
	Isopropanol	0.112	0.28×10^{-3}	
	Methyl ethyl ketone	0.171	0.85×10^{-3}	
	TVOCs	0.394	–	
	Formaldehyde	0.413	0.55	
	Ozone	1.154	11.54	
SPF 2	Toluene	0.107	0.54×10^{-3}	0.12
	Ethylbenzene	1.705	0.02	
	p,m-xylene	8.266	0.08	
	o-xylene	0.959	9.59×10^{-3}	
	Isopropanol	0.072	0.18×10^{-3}	
	Acetone	0.134	0.13×10^{-3}	
	Methyl ethyl ketone	0.219	1.10×10^{-3}	
	TVOCs	11.462	–	
	Formaldehyde	0.010	0.01	
	Ozone	0.810	8.1	
SPF 3	Benzene	0.022	0.02	0.95
	Toluene	35.459	0.18	
	TVOCs	35.480	–	
	Formaldehyde	0.564	0.75	
	Ozone	3.997	39.97	
SPF 4	Acetone	0.013	0.01×10^{-3}	0.60
	Isopropanol	0.061	0.15×10^{-3}	
	Toluene	4.854	0.02×10^{-3}	
	TVOCs	4.928	–	
	Formaldehyde	0.451	0.60	
	Ozone	3.265	32.65	
SPF 5	Toluene	0.427	2.14×10^{-3}	1.21
	Ethylbenzene	3.903	0.04	
	p,m-xylene	28.276	0.28	
	o-xylene	1.503	0.02	
	Isopropanol	0.194	0.49×10^{-3}	
	Acetone	0.525	0.53×10^{-3}	
	Methyl ethyl ketone	0.201	1.01×10^{-3}	
	TVOCs	35.029	–	
	Formaldehyde	0.650	0.87	
	Ozone	0.650	6.50	

Ozone was mostly generated as the by-product of the printing process of UV and thermal curing of the inks. For these reasons the ozone concentrations in investigated screen printing facilities varied from 0.650 to 3.997 ppm and they differ from each other almost 1.5 to 6 times. The reason why the ozone concentration varies is probably due to the airflow around the printer, diffusion of ozone in the air, the characteristic of ozone monitor used in this study or ozone reaction with other VOCs in the air. High concentrations of ozone generated at the printing plant pointed out to the pollution of ambient air, because the ozone may oxidize VOCs into other contaminants, such as aldehydes, acids etc.

It is necessary to monitor not only VOCs but also aldehydes such as formaldehyde in indoor air. The concentration of formaldehyde varies from 0.01 to 0.8 ppm in various facilities. The average exposure concentration (AEC) values of VOCs, formaldehyde and ozone are presented in Table 2. Detected and quantified concentrations of organic compounds (individual and total VOCs and formaldehyde) confirmed that printing raw materials (printing ink, cleaning solution and adhesive) are the main emission sources of organic components in screen printing indoor. More than 65% of total formaldehyde is used to synthesize resins including urea-formaldehyde (UF), phenol-formaldehyde (PF), and melamine-formaldehyde (MF), which are often found in printing raw materials (inks, binders, coating and adhesives) that contribute directly to indoor formaldehyde pollution [34]. This is mainly due to the stronger sources and lower air exchange in the indoor environment.

The average exposure concentrations of individual and total volatile organic compounds over 4 h were calculated by Eq. (5) [35]:

$$AEC=(C_1T_1+C_2T_2+\cdot+C_nT_n)/(T_1+T_2+\cdot+T_n) \quad (5)$$

where: C_n is the concentration measured in the workplace; T_n is the time of the sampling period (40 min); 1, 2,…, n are indications of the sampling period and

$$T_1+T_2+\ldots+T_n=240\ \text{min}(4\ \text{h}).$$

The effect of an indoor air pollutant is measurable or perceivable. The combined effect of measurable or perceivable pollutants may be additive, synergistic, antagonistic or independent [36]. Due to the exposure to a single organic and inorganic substance and a mixture of substances the adverse health effects can be determined by the individual effect (IE_i) and the additive effect (AE), respectively, expressed by Eqs. (6) and (7) [37]:

$$IE_i=AEC_i/PEL_i \quad (6)$$

$$AE=\sum_i IE_i=\sum_i AEC_i/PEL_i \quad (7)$$

where AEC_i and PEL_i are average exposure concentrations of VOCs, formaldehyde and ozone measured during 4 h and their Permissible Exposure Limit (PEL) prescribed by Occupational Safety and Health Administration (OSHA) standards [38], respectively.

The extensive use of multiple organic solvents in screen printing causing high emissions of volatile organic compounds (VOCs) indeed poses a serious risk to the workers' health. The measurements showed that although a variety of organic pollutants (VOCs) were detected in the screen printing environment, none of them were close to the permissible exposure limit. However, the additive effect in SPF 5 (1.21) was found to be above the critical value (1) [36]. Ozone, as an inorganic pollutant, exceeded the maximum allowed concentration (MAC) values in all the investigated SPFs. Its individual effect is very high in comparison with the individual effects of detected VOCs.

The individual and additive effects are the indicators of the linear dependence between the real measured concentrations of the air pollutants in indoor environment and workers' health. The precise effect of pollutants on health is virtually difficult to obtain, because individual differences in humans are significant. The effects depend on the genetic make-up, health, history of exposure, preconditioning and pollutant reaction time. The health studies are generally conducted to develop cause and affect relationships.

Table 3
MACs for individual VOCs, formaldehyde and ozone.

Substances	MAC (ppm)			
	OSHA		NIOSH	
	PEL	STEL	REL	IDLH
Acetone	1000	1000	250	2500
Isopropanol	400	500	400	2000
Methyl ethyl ketone	200	300	200	3000
Benzene	1	5	0.1	500
Ethylbenzene	100	125	100	800
Toluene	200	300	100	500
o-xylene	100	150	100	900
p,m-xylene	100	150	100	900
Formaldehyde	0.75	2	0.016	20
Ozone	0.1	0.3	0.1	5

When many pollutants are present at low concentration levels in indoor air, their combined health effects on individuals are not predictable with the toxicological knowledge. The preferred method for indoor air quality management is the control of the pollution sources. The choice methods for controlling the dominant sources are source removal/replacement, isolation and local ventilation [36].

Several safety and occupational health authorities worldwide have suggested permissible exposure levels of VOCs, formaldehyde and ozone. The OSHA has prescribed the PEL and the Short-Term Exposure Limit (STEL) [38]. Also, the National Institute for Occupational Safety and Health (NIOSH) has set a Recommended Exposure Limit (REL) and a more stringent Immediately Dangerous to Life and Health (IDLH) for occupational exposure of VOCs, formaldehyde and ozone [39]. The MACs for detected individual VOCs, formaldehyde and ozone are presented in Table 3.

By comparing the TVOCs, formaldehyde and ozone concentrations it was confirmed the existence of mutual dependences between them.

Namely, the presence of higher formaldehyde concentrations and lower TVOCs concentrations in SPFs 1 and 4 could be explained by the fact that TVOCs in the presence of ozone generate formaldehyde (Fig. 5). In the case of screen printing facility 3, the opposite effect was observed. The high TVOCs concentrations in the screen printing workplace are caused by the usage of conventional "high-VOC" liquid materials for the cleaning process. Whereas, the values of TVOCs and formaldehyde were the same in screen printing facility 5.

When the correlation between TVOCs and ozone was observed (Fig. 6), the trend of their mutual dependence is the same in SPFs 2 and 3. However, the opposite dependence was observed in screen printing facilities 1 and 4, as in Fig. 5, where the TVOCs concentration is lower than the ozone concentration.

The opposite mutual dependence of formaldehyde and ozone concentrations was observed in SPFs 1 and 5 (Fig. 7). Whereas, the same trend of mutual dependence of ozone and formaldehyde concentrations is gotten in SPFs 2, 3 and 4.

Therefore, increased concentrations of formaldehyde in facility 1 and 5 were caused by a significant increase in temperature and relative humidity [22,40].

Regression analysis is used for the identification of variables. It was predeterminated that X is time and Y is concentration of organic pollutants. The aim of regression analysis was to determine the nature of relationship and a form of dependence between the observed phenomena. For this purposes the regression model was used because it best expresses the quantitative dependence of the studied phenomenon.

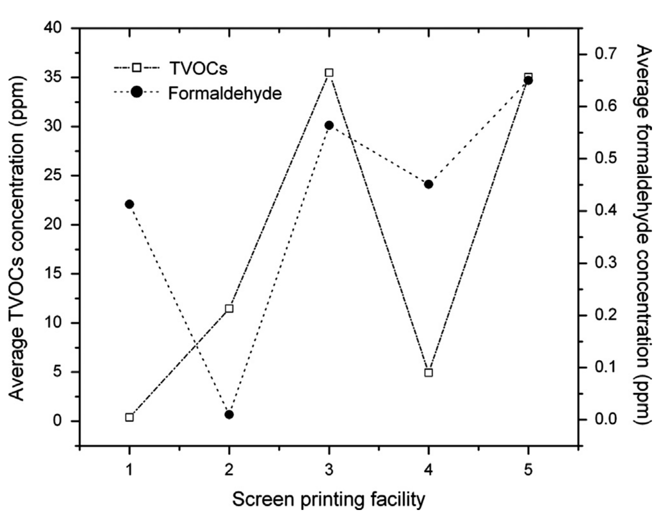


Fig. 5. Correlation between TVOCs and formaldehyde.

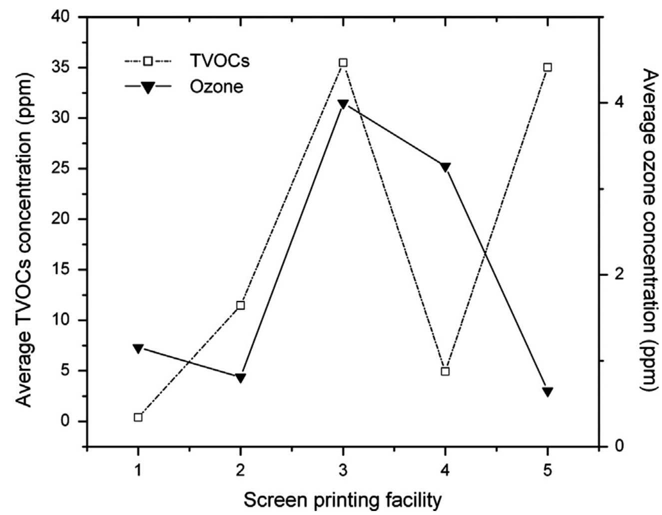


Fig. 6. Correlation between TVOCs and ozone.

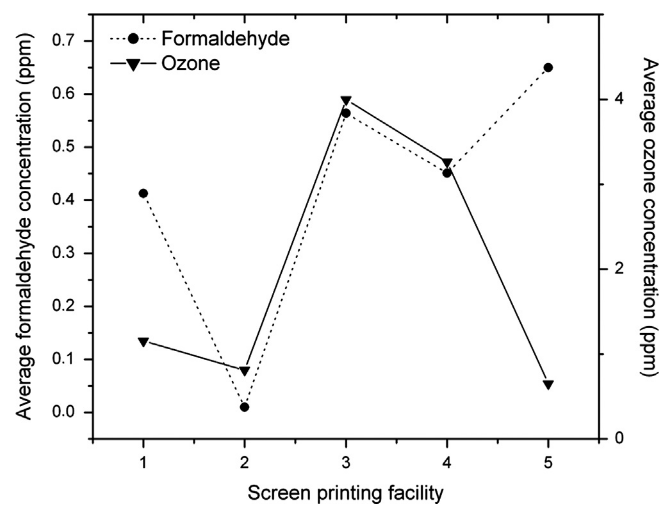


Fig. 7. Correlation between formaldehyde and ozone.

Independent variable (time) and dependent variable (concentration of organic pollutants) were defined for the correlation analysis. The aim of the correlation analysis is to determine a quantitative agreement (correlation) among the observed phenomenon and the strength of the agreement. Software package ORIGIN 5.0. was used for the data processing. SPF 3 was excluded from the analysis due to the small dataset. The results of regression analysis obtained for SPFs 1, 2, 4 and 5 are presented in Tables 4–7.

The obtained values of Pearson′s coefficient were negative for all measured concentrations of organic pollutants in SPFs 1 and 4. Lower values of dependent variable Y correspond to a higher values of independent variables X and vice versa. Values of Pearson′s coefficient in SPF 2 were very high in amount of 0.99464, 0.97192, 0.96791 and 0.94949 for *p*,*m*-xylene, TVOCs, acetone and methyl ethyl ketone, respectively. The highest value of Pearson′s coefficient in SPF 5 had toluene, acetone, ethylbenzene and xylene (0.98439, 0.94321, 0.93087 and 0.90024, respectively). These values indicate a strong correlation between the observed phenomena. A significant correlation is obtained between time and ethylbenzene (0.89719, SPF 2), *o*-xylene (0.84189, SPF 2), *p*,*m*-xylene (0.85311, SPF 5) and TVOCs (0.87093, SPF 5). Moderate

Table 4
The results of regression analysis, SPF 1.

Organic pollutant	Pearson coefficient	SD	p	Regression model
Acetone	−0.56340	0.01279	0.24431	$Y=0.12493–1.04286\times10^{-4}\,X$
Isopropanol	−0.03031	0.00985	0.95455	$Y=0.11267–3.57143\times10^{-6}\,X$
Methyl ethyl ketone	−0.41597	0.0405	0.41203	$Y=0.202–2.21429\times10^{-4}\,X$
TVOCs	−0.42248	0.0591	0.40398	$Y=0.4396–3.29286\times10^{-4}\,X$

Table 5
The results of regression analysis, SPF 2.

Organic pollutant	Pearson coefficient	SD	p	Regression model
Toluene	−0.28873	0.25881	0.57895	$Y=0.26893–9.32857\times10^{-4}\,X$
Ethylbenzene	0.89719	0.38011	0.01531	$Y=0.10573+0.00923\,X$
p,m-xylene	0.99464	0.34532	<0.0001	$Y=1.3824+0.03971\,X$
o-xylene	0.84189	0.24578	0.03552	$Y=0.1644+0.00458\,X$
Isopropanol	0.90839	0.02558	0.0122	$Y=-0.04333+6.64286\times10^{-4}\,X$
Acetone	0.96791	0.01210	0.00153	$Y=0.03733+5.57143\times10^{-4}\,X$
Methyl ethyl ketone	0.94949	0.02007	0.00376	$Y=0.09307+7.25714\times10^{-4}\,X$
TVOCs	0.97192	1.10468	0.00117	$Y=2.00853+0.05454\,X$

Table 6
The results of regression analysis, SPF 4.

Organic pollutant	Pearson coefficient	SD	p	Regression model
Acetone	−0.69790	0.01220	0.12311	$Y=0.0324–1.42143\times10^{-4}\,X$
Isopropanol	−0.26392	0.05853	0.61332	$Y=0.08747–1.91429\times10^{-4}\,X$
Toluene	−0.12395	11.0110	0.81502	$Y=7.15593–0.01644\,X$
TVOCs	−0.12655	11.0006	0.81119	$Y=7.2758–0.01677\,X$

Table 7
The results of regression analysis, SPF 5.

Organic pollutant	Pearson coefficient	SD	p	Regression model
Toluene	0.98439	0.04045	3.63507×10^{-4}	$Y=-0.04193+0.0027\,X$
Ethylbenzene	0.93087	1.22773	0.07	$Y=-2.57773+0.03739\,X$
p,m-xylene	0.85311	15.2849	0.03078	$Y=-23.50433+0.29873\,X$
o-xylene	0.90024	0.62026	0.01443	$Y=-1.154+0.01533\,X$
Isopropanol	0.47685	0.04120	0.33894	$Y=0.1476+2.67143\times10^{-4}\,X$
Acetone	0.94321	0.12597	0.00475	$Y=-0.216+0.00428\,X$
Methyl ethyl ketone	0.59847	0.04016	0.20947	$Y=Y=0.13913+3.58571\times10^{-4}\,X$
TVOCs	0.87093	16.9497	0.02391	$Y=-27.20727+0.35905\,X$

correlation occurs between time and methyl ethyl ketone (0.59847) and isopropanol (0.47685) in SPF 5.

p-value was in range from 0.12311 to 0.95455 in SPFs 1 and 4, and thus the hypothesis H_0 is accepted. This hypothesis states that all coefficients are equal ($\sigma_1=\sigma_2=\sigma_3=0\ldots$) [41]. Obtained results were not statistically significant and independent variable (time) does not affect the dependent variable (concentration of organic pollutants).

p-value in SPFs 2 and 5 was less than 0.05 with exception for toluene (SPF 2) and ethyl benzene, isopropyl alcohol, methyl ethyl ketone (SPF 5). Therefore, the alternative hypothesis H_1 is accepted [41]. The influence of independent variable (time) on the dependent variable (concentration of organic contaminants) was statistically significant.

4. Conclusions

Research conducted in this paper is a contribution to understanding the impact of harmful emissions that occur in the process of printing on workers health. Determined concentrations of certain gases indicate not only their presence, but also the fact that their level exceeds the value of the OSHA and NIOSH standards.

The findings obtained in this study significantly enhance our understanding on the levels, emission sources and factors which affect indoor concentrations of VOCs, formaldehyde and ozone. In SPF 3 the concentration levels of benzene and toluene exceeded 1.30 and 172 times REL values prescribed by NIOSH, respectively. The detected concentration levels of ozone in all screen printing facilities much exceeded 0.1 ppm (from 6.50 to 39.97 times) prescribed by the OSHA and NIOSH standards.The individual effects of ozone in all investigated SPFs were much higher in comparison with the individual effects of detected VOCs. The individual VOCs presented in indoor air of SPF 5 contributed to the higher additive effect ($AE>1$). But, it is not the case for all other printing facilities.

Besides individual and total VOCs and ozone, certain concentrations of formaldehyde were detected in all investigated screen printing facilities. The obtained formaldehyde concentrations varied

from 0.01 to 0.8 ppm. The presence of organic compounds (individual and total VOCs and formaldehyde) confirmed that used printing materials are the main emission sources in indoor air. Further more, urea-formaldehyde, phenol-formaldehyde and melamine-formaldehyde, which are often found in printing raw materials (inks, binders, coating and adhesives), contributed directly to indoor formaldehyde pollution.

The results confirmed the existence of the mutual dependence between TVOCs, formaldehyde and ozone concentrations. When the ozone and formaldehyde concentrations increased (SPFs 1 and 4) the TVOC concentrations decreased. This phenomenon can be explained by the fact that TVOCs in presence of ozone generate formaldehyde. The opposite mutual dependence of formaldehyde and ozone concentrations was observed in SPF 3. Therefore TVOCs concentrations were higher, due to usage of conventional "high-VOC" liquid materials for cleaning process.

The correlation analysis, using multiple linear regression, determined a quantitative agreement among the observed phenomenon and the strength of the agreement. Obtained results were not statistically significant and independent variable (time) does not affect the dependent variable (concentration of organic pollutants). In investigated facilities SPFs 1 and 4 p-value was in range from 0.12311 to 0.95455, and thus the hypothesis H_0 is accepted. On the other side, p-value in SPFs 2 and 5 was less than 0.05 with exception for toluene (SPF 2) and ethyl benzene, isopropyl alcohol, methyl ethyl ketone (SPF 5). Therefore, the alternative hypothesis H_1 is accepted. The influence of time on the concentration of organic contaminants was statistically significant.

The quantitative information about the trend of the indoor air organic and inorganic compounds will be useful for the risk assessment of indoor exposure to those compounds, and also for the creation of IAQ guidelines of the Republic of Serbia.

The further study of the emission sources in a wide range of occupational environments as well as the measurements of the exposure levels at the employees' could be significant for knowledge and could help the development of the strategies for a healthier working environment.

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